PEER REVIEW

# Preliminary Survey of the Chemical Parameters of Streams Draining the Adirondack High Peaks, New York

By JEFFREY R. CHIARENZELLI

**Abstract**

*Stream water chemistry in the High Peaks of the Adirondack Park is largely unknown but is of concern because of chronic acidification of the region, the limited capacity of bedrock to buffer acidity, and corresponding changes to natural systems (i.e. biota, soil nutrients, water chemistry, etc.). In order to develop a baseline dataset from which future changes can be evaluated, seventeen streams in the High Peaks were sampled over a two-day period for multi-element concentration, pH, and acid neutralizing capacity. The streams are dilute and have a variable, but generally low, capacity to neutralize acidity but were only moderately acidic during this sampling event (pH 5.74 ± 0.50). They have silicon and calcium as their dominant cations and are enriched in aluminum. While stream chemistry is controlled by hydrolysis of plagioclase feldspar and pH, some streams were well buffered with near neutral pH values. Differences in stream chemistry most likely reflect the presence or absence of calcium-rich minerals in xenoliths entrained within the meta-igneous bedrock. With limited soil development, short water retention times, and anorthositic bedrock, drainage basins in the High Peaks region will likely respond quickly to future geochemical changes affecting the entire region.*

Key Words: *High Peaks, stream chemistry, massif anorthosite, Adirondack Park, New York*

## Introduction

The Adirondack Park is a six million acre patchwork of public and private land within what has been historically termed the Adirondack Blue Line. From a regulatory perspective, the Blue Line demarks the jurisdiction of the Adirondack Park Agency; however, from a geological perspective, it closely follows the domal exposure of Precambrian crystalline rocks that range in age from 1000 to 1350 million years old (McLelland et al. 1988). One of the first experiments in public land acquisition, the Park has been often cited as an example of how the preservation of other relatively undeveloped areas of public and private land might be structured and the numerous difficulties encountered in such an arrangement (Jenkins & Keal, 2004; Schneider, 1997; Terrie, 1997). Despite its location within a day's drive of millions of people in various urban centers, the park has extensive wilderness areas and a limited human population (Jenkins & Keal, 2004). As a consequence, major pollution threats to the Park are generally considered to be external. Among these acid precipitation (Jenkins et al. 2007) and far-traveled contaminants, such as mercury, are considered to be of the most concern and perhaps linked (Brown et al. 2010).

Jeffrey R. Chiarenzelli is James Henry Chapin Professor of Geology and Mineralogy at St. Lawrence University. He may be contacted at jchiaren@stlawu.edu.

Landmark studies on the acidification of Adirondack lakes were initially carried out by the Adirondack Lakes Survey Corporation (ALSC) from 1984 to 1987 and monitoring of select lakes continues. The goals of the ALSC study included determining how many and which lakes had become acidified and the effects on fish populations (Baker et al. 1993; Kretser et al. 1989). Some evidence suggests that considerable progress has been made in reducing sulfur deposition through the nationwide reductions in the use of high sulfur fuels (Driscoll et al. 2003). However, changes in nitrogen ($NO_x$) deposition have been minimal at best and the deposition of acidic chemical species remains a considerable challenge in the region (Jenkins et al. 2007).

As a consequence, acidification and deleterious effects on aquatic life persist in a number of waterways in the Adirondack region (Baker et al. 1993; Driscoll et al. 2003; Jenkins et al. 2007; Lawrence, 2002; Lawrence et al. 2004; 2008). Recent work has recognized the episodic acidification of some streams and rivers (Chiarenzelli et al. 2012; Jenkins et al. 2007; Lawrence, 2002; Lawrence et al. 2004; 2008). Most of the acidified water bodies occur in the western part of the Adirondack region (Chiarenzelli et al. 2012; Jenkins et al. 2007; Lawrence, 2002; Lawrence et al. 2004; 2008) where air masses from midwestern sources deposit acidic compounds, among other contaminants (Chiarenzelli et al. 2006), perhaps enhanced by lake-effect precipitation (Chiarenzelli et al. 2002). Here the first multi-element study of stream chemistry in the Adirondack High Peaks region is summarized.

## Geological Setting

The Adirondack region is a small part of an extensive linear belt of rocks which form the deep crustal root of a billion-year-old and highly eroded mountain belt. Rocks of the contiguous Grenville Province extend from Greenland,

along eastern Canada primarily in Quebec and Ontario, into the Adirondacks, and then occur in a series of basement inliers in the Appalachian Mountains (Fig. 1). Metamorphic assemblages indicate the rocks now exposed at the surface were tectonically buried by as much as 30 kilometers of overlying crust during a series of mountain building events culminating at 1050 Ma (McLelland et al. 1996). The Adirondack region consists of an oval, north-northeast-trending, erosional window exposing the older (ca. 1000–1350 Ma) basement rocks that underlie most of New York State. Elsewhere they are covered by a relatively thin veneer of younger Paleozoic sedimentary rocks.

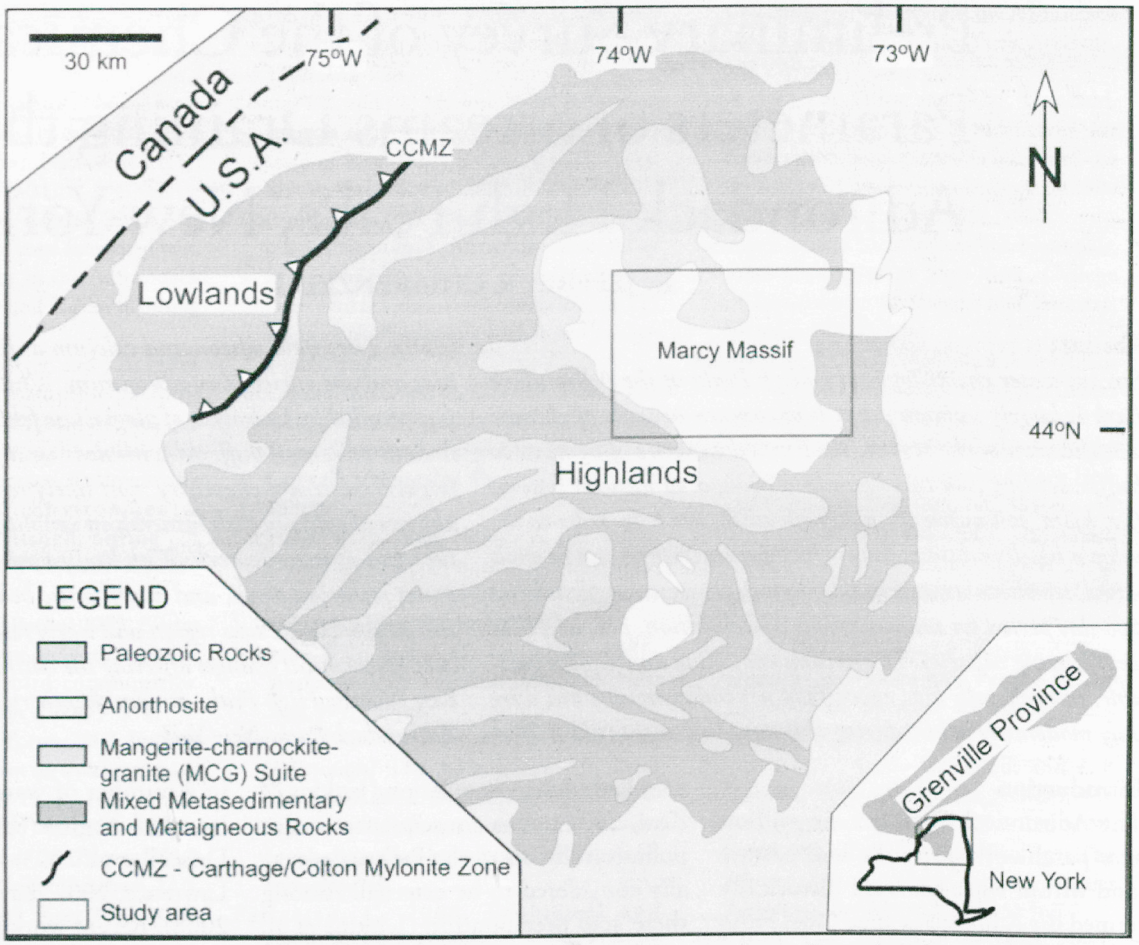


**Figure 1.** *Map of northern New York showing the extent of basement rocks that make up the Adirondack Mountains and its simplified geology. Inset shows location of the Adirondacks with respect to the greater contiguous Grenville Province and the boundaries of New York State. The study area is shown in the rectangle and expanded in Figure 2.*

By approximately 500 Ma, the region was worn down to sea level and Cambrian and Ordovician sedimentary rocks of marine affinity blanketed the older Mesoproterozoic basement rocks now exposed in the Adirondack region. The rocks of the Adirondack region were subsequently exhumed by doming and uplift which began nearly 180 million years ago (Roden-Tice & Tice, 2005). Doming resulted in the erosional removal of the Lower Paleozoic sedimentary rocks and their unconformable contact with the underlying Precambrian basement rocks can be observed along the edge of the Adirondack dome. This uplift is thought related to thermal effects of continental movement over the Great Meteor hotspot (Taylor & Fitzgerald, 2011). The region's seismicity, radial drainage, and past re-leveling surveys suggest uplift continues (Isachsen, 1975; 1981).

The High Peaks region forms the center of the Adirondack domal exposure of Mesoproterozoic rock and is underlain primarily by an exceptionally coarse, monominerallic (>90% plagioclase feldspar), crystalline rock known as massif anorthosite (Buddington, 1939; Isachsen & Fisher, 1970). Massif anorthosite is found almost exclusively in the Mesoproterozoic Grenville Province and thus has a relatively limited spatial and temporal occurrence. Because it has been subjected to high temperatures and pressures deep within the roots of a mountain belt it is technically a metamorphosed igneous rock. However, original igneous textures and contact relations with other rock units are readily observed and often the only indication of high-grade metamorphism is the garnet grown during metamorphism.

Massif anorthosite, composed almost entirely of plagioclase feldspar of andesine composition, is spatially associated with a suite of metamorphosed igneous rocks collectively known as the anorthosite-mangerite-charnockite-granite (AMCG) suite. In addition, anorthosite grades into gabbroic rocks with increased mafic-mineral content (Buddington, 1939). Massif anorthosite is believed to have formed by the crystallization and separation of plagioclase from mantle-derived magmas ponded at the base of the crust (McLelland et al. 2010; Regan et al. 2011). These mafic magmas

were intruded at 1150–1160 Ma following a mountain building event known as the Shawinigan Orogeny (Regan et al. 2011). Because of the high temperature of mantle melts, the lower crust in contact with the mafic magmas also melted to yield the felsic igneous rocks (MCG) found in and around the Marcy Massif. Often the entire AMCG suite shows mutual cross-cutting relations indicating they formed contemporaneously, whereas, their composition and isotopic systematics indicate they have distinct crustal (mangerite, charnockite, and granite) and mantle (anorthosite and gabbro) sources (McLelland et al. 1996; 2010; Regan et al. 2011).

Our goal in this study was to capitalize on a unique sampling opportunity to take a "snapshot" of water chemistry in streams in the High Peaks region during a single sampling event. Since the High Peaks region is the headwaters for many of northern New York's major rivers, is underlain almost exclusively by anorthosite and related rocks with moderate to limited buffering capacity, has only sporadic glacial cover and soil development, and is upstream of practically all local human influence, we hypothesized that the water chemistry would largely reflect the influence of precipitation. To test this, the chemistry of streams draining the High Peaks region and their capacity to buffer acidity was investigated.

The preliminary data serves as a baseline for any future work designed to investigate changes in stream water chemistry due to external factors such as changes in environmental regulations, emissions from powerplants or transportation, energy policies/use, global climate, atmospheric composition, precipitation, and population (e.g. Chiarenzelli, 2008; Driscoll et al. 2003; Jenkins et al. 2007; McKibben, 2002; Stager & Martin, 2002). It is also one of the few studies to address acidification of streams, aside from work in the western Adirondacks (Lawrence, 2002; Lawrence et al. 2004; 2008), and the only one to do so in the High Peaks region.

## Methodology

This study was designed to provide baseline geochemistry information for streams in the High Peaks region utilizing a unique sampling opportunity carried out by volunteers. Samples were collected during a two-day period in early October, 2008 in association with St. Lawrence University's Outing Club's Peak Weekend. The goal of the decades-old activity is to put St. Lawrence students, alumni, and staff on all of the 46 High Peaks whose elevation is greater than 1219 m (4000′) during the course of the weekend (Fig. 2). Using routes selected

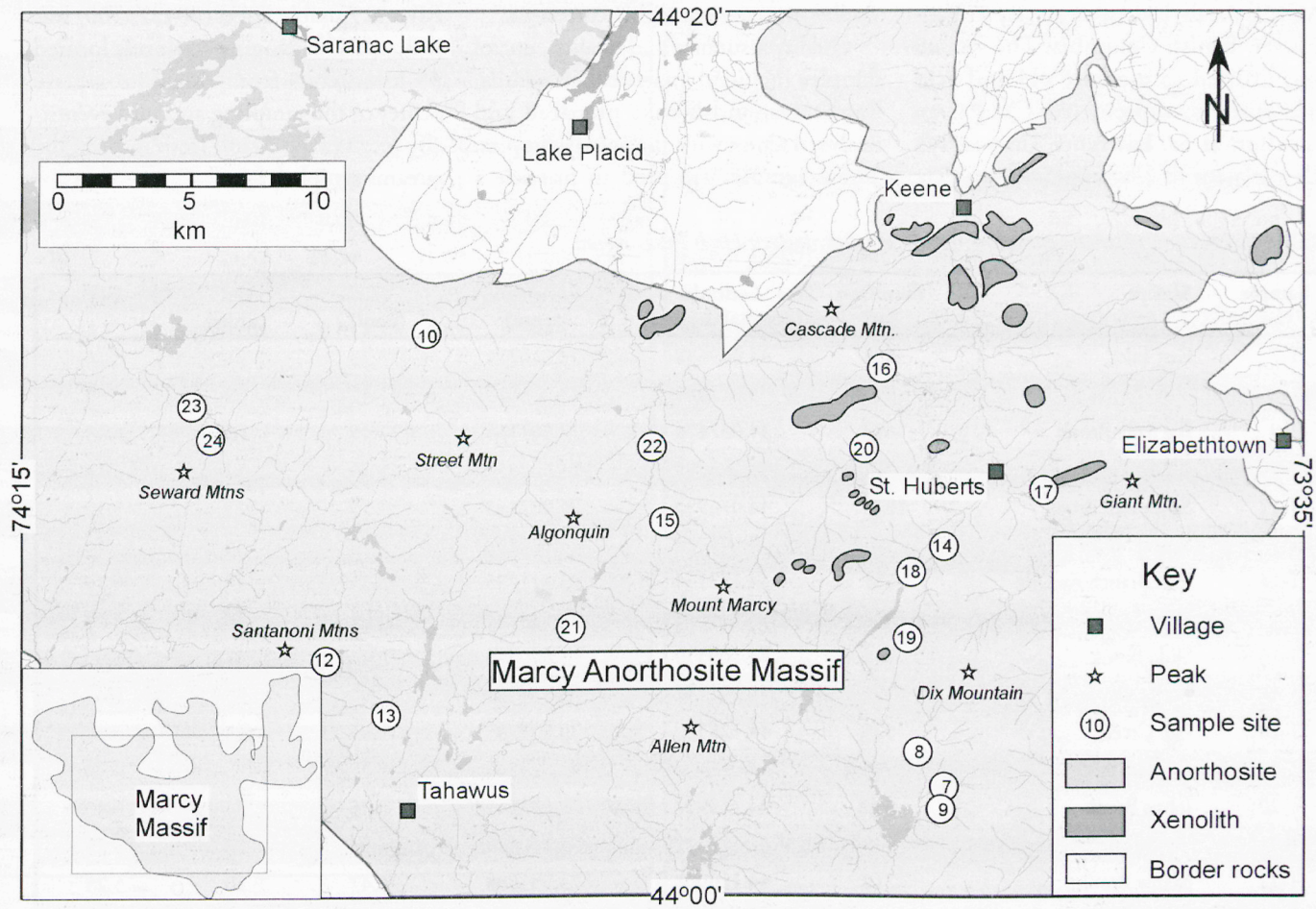


**Figure 2.** *Location diagram showing the sampling sites utilized in this study, drainages and lakes, select peaks, and geology after Isachsen & Fisher (1970). Inset shows the entire Marcy Anorthosite Massif while the rectangle shows the area displayed in detail in this figure.*

for peak ascent, specific stream crossing sites (Table 1) were chosen to provide a reasonable geographic coverage of the region's streams. Each group of four or more participants had a trip leader responsible for the sampling event.

A training session was held to ensure each group knew how and where to sample. Each group was assigned two pre-cleaned, metals-certified, plastic 150 mL Wheaton Clean-pak® containers which were filled directly from the stream at a depth of approximately 5 cm. Samples were sealed and placed in backpacks without preservation or filtration of any type. Modified chain-of-custody forms where utilized and each sample container had a unique six number sample identifier and bar code to ensure samples were not misidentified or mislocated. One container was designated for Inductively Coupled Plasma-Mass Spectromety (ICP-MS) analysis at ACME Analytical Laboratories in Vancouver, British Columbia. The second was utilized to measure pH and acid neutralization capacity (ANC) by Gran titration at St. Lawrence University's Department of Geology. Samples were collected and those intended for multi-element analysis were shipped to ACME Analytical Laboratory. Samples collected for pH and ANC measurement were refrigerated in the dark and analyzed within one week of collection.

Multi-element ICP-MS data for 72 elements (Table 2) were entered into a Microsoft Excel spreadsheet. The total dissolved solids (TDS) were calculated by the summation of the detected concentrations of each element. The spreadsheet was used to calculate the mean, standard deviation, and to list the number of detectable concentrations and the range of values in each sample. Correlation coefficients were calculated to compare the concentrations of each element to the others. Correlation coefficients provide a numeric measure of the degree to which the concentrations of elements are correlated (Table 3). Generally those with similar geochemical properties or affected by similar processes are highly correlated.

Quality assurance and quality control samples included analytical standards, duplicates, and blanks prepared and analyzed along with the actual samples. These samples are used to provide a quantitative measure of how accurate and precise the data are and whether or not it has been impacted by laboratory contaminants, sample handling, or analytical procedures. Relative percent difference (RPD) was calculated and used to assess how accurate the data were using a certified multi-element water standard that was analyzed along with the stream samples (Table 2). These data were compared to, and consistent with, the results of over ten years' quality assurance data reported in detail elsewhere (see Chiarenzelli et al. 2012 and references within).

Weather conditions during the sampling period, specifically temperature and rainfall, were obtained from the Saranac Lake Airport (elevation 507m), the closest weather station with archival records. Water discharge data from the nearest United States Geological Survey (USGS) gauging station on the Ausable River at Ausable Forks (#04275500) was utilized. The gauging station is located 35 kilometers from the approximate center of the sampling area and eventually receives the runoff from most of the streams sampled.

**Table 1.** *Location of stream sampling sites in the Adirondack High Peaks region*

| Sample | Stream | Elevation (m) | Latitude (decimal degrees) | Longitude (ppm) | TDS (µeq/L) | ANC (units) | pH |
|---|---|---|---|---|---|---|---|
| JT-7 | East Inlet | 685 | 44.069638 | 73.810711 | 8.73 | 31 | 6.26 |
| JT-8 | Slide Brook | 850 | 44.047759 | 73.795070 | 11.35 | 69 | 6.30 |
| JT-9 | Big Sally Brook | 683 | 44.037474 | 73.807165 | 11.49 | 69 | 6.19 |
| JT-10 | Indian Pass Brook | 711 | 44.186389 | 74.002552 | 9.36 | 57 | 6.18 |
| JT-12 | Santanoni Brook | 1077 | 44.076903 | 74.087143 | 7.19 | 25 | 5.10 |
| JT-13 | Santanoni Brook | 594 | 44.095187 | 74.125432 | 7.10 | 30 | 5.44 |
| JT-14 | East Branch Ausable | 551 | 44.133144 | 73.811785 | 8.35 | 44 | 5.78 |
| JT-15 | Trib. To Arnold Lake | 1046 | 44.136316 | 73.938717 | 6.22 | 36 | 5.26 |
| JT-16 | Slide Brook | 586 | 44.169550 | 73.840476 | 8.43 | 57 | 6.09 |
| JT-17 | Porter Brook | 578 | 44.151136 | 73.751923 | 12.97 | 95 | 6.42 |
| JT-18 | Gill Creek | 525 | 44.128530 | 73.807795 | 7.85 | 23 | 5.77 |
| JT-19 | Gill Creek | 990 | 44.098157 | 73.824349 | 7.25 | 9 | 4.90 |
| JT-20 | Johns Brook | 609 | 44.173937 | 73.838505 | 16.06 | 83 | 6.30 |
| JT-21 | Opalescent Creek | 993 | 44.110127 | 73.960400 | 6.64 | 17 | 5.29 |
| JT-22 | Marcy Brook | 719 | 44.156908 | 73.953898 | 6.47 | 16 | 5.25 |
| JT-23 | Ward Brook | 648 | 44.175669 | 74.169506 | 8.08 | 30 | 5.75 |
| JT-24 | Trib. To Ward Brook | 626 | 44.186065 | 74.201331 | 7.45 | 20 | 5.34 |

**Table 2.** *Summary of stream water chemistry results for streams in the Adirondack High Peaks region. The major components of the streams are silicon, calcium, sodium, magnesium, and aluminum. DL – detection limit; Count – number of times detected out of 18; Mean – mean value; Std. Dev. – standard deviation; High – highest concentration; Low – lowest concentration; RPD – relative percentage difference; nd – non-detect; na – not applicable.*

| | DL (µg/L) | Count | Mean (µg/L) | Std. Dev. (µg/L) | High (µg/L) | Low (µg/L) | RPD (%) |
|---|---|---|---|---|---|---|---|
| Ag | <.05 | 0 | nd | nd | nd | nd | |
| Al | <1 | 18 | 261.1 | 166.9 | 562.0 | 54.0 | 6.81 |
| As | <.5 | 0 | nd | nd | nd | nd | |
| Au | <.05 | 0 | nd | nd | nd | nd | |
| B | 5 | 1 | 5.00 | nd | 5.00 | 5.00 | |
| Ba | <0.05 | 18 | 3.26 | 0.88 | 4.60 | 1.73 | 0.69 |
| Be | <.05 | 0 | nd | nd | nd | nd | |
| Bi | <.05 | 0 | nd | nd | nd | nd | |
| Br | <5 | 0 | nd | nd | nd | nd | |
| Ca | <50 | 18 | 2076.9 | 922.8 | 4098.0 | 1061.0 | 9.09 |
| Cd | <.05 | 7 | 0.07 | 0.01 | 0.08 | 0.06 | 0.00 |
| Ce | <0.01 | 18 | 0.09 | 0.04 | 0.16 | 0.03 | 0.00 |
| Cl | <1000 | 1 | 3000.0 | nd | 3000.0 | 3000.0 | |
| Co | <0.02 | 13 | 0.14 | 0.09 | 0.33 | 0.02 | 5.71 |
| Cr | <.5 | 6 | 0.75 | 0.23 | 1.10 | 0.50 | |
| Cs | <.01 | 2 | 0.01 | 0.00 | 0.01 | 0.01 | |
| Cu | <.1 | 3 | 0.33 | 0.40 | 0.80 | 0.10 | |
| Dy | <.01 | 15 | 0.01 | 0.00 | 0.02 | 0.01 | 0.00 |
| Er | <.01 | 9 | 0.01 | 0.00 | 0.01 | 0.01 | |
| Eu | <.01 | 7 | 0.01 | 0.00 | 0.01 | 0.01 | 0.00 |
| Fe | <10 | 7 | 24.57 | 11.39 | 41.00 | 10.00 | 30.99 |
| Ga | <.05 | 0 | nd | nd | nd | nd | |
| Gd | <.05 | 18 | 0.01 | 0.01 | 0.03 | 0.01 | 0.00 |
| Ge | <.05 | 0 | nd | nd | nd | nd | |
| Hf | <.02 | 0 | nd | nd | nd | nd | |
| Hg | <.1 | 5 | 0.10 | 0.00 | 0.10 | 0.10 | |
| Ho | <.01 | 0 | nd | nd | nd | nd | |
| In | <.01 | 0 | nd | nd | nd | nd | |
| Ir | <.05 | 0 | nd | nd | nd | nd | |
| K | <50 | 11 | 122.0 | 70.3 | 233.0 | 50.0 | |
| La | <0.01 | 18 | 0.04 | 0.02 | 0.09 | 0.02 | 0.00 |
| Li | <.1 | 5 | 0.10 | 0.00 | 0.10 | 0.10 | |
| Lu | <.01 | 0 | nd | nd | nd | nd | |
| Mg | <50 | 18 | 304.3 | 174.5 | 701.0 | 123.0 | 9.30 |
| Mn | <.05 | 13 | 7.71 | 4.57 | 12.75 | 0.06 | 3.27 |
| Mo | <.1 | 0 | nd | nd | nd | nd | |
| Na | <50 | 18 | 768.9 | 597.7 | 3024.0 | 372.0 | 8.99 |
| Nb | <.01 | 0 | nd | nd | nd | nd | |
| Nd | <0.01 | 18 | 0.07 | 0.03 | 0.16 | 0.03 | 0.00 |
| Ni | <.2 | 0 | nd | nd | nd | nd | |
| Os | <.05 | 0 | nd | nd | nd | nd | |
| P | <20 | 0 | nd | nd | nd | nd | |
| Pb | <.1 | 0 | nd | nd | nd | nd | |
| Pd | <.2 | 0 | nd | nd | nd | nd | |
| Pr | <0.01 | 18 | 0.01 | 0.01 | 0.03 | 0.01 | 0.00 |
| Pt | <.01 | 0 | nd | nd | nd | nd | |
| Rb | <0.01 | 18 | 0.19 | 0.13 | 0.57 | 0.05 | 0.00 |
| Re | <.01 | 0 | nd | nd | nd | nd | |
| Rh | <.01 | 0 | nd | nd | nd | nd | |
| Ru | <.05 | 0 | nd | nd | nd | nd | |
| S | <1000 | 18 | 1333.3 | 485.1 | 2000.0 | 1000.0 | 0.00 |
| Sb | <.05 | 4 | 0.07 | 0.00 | 0.07 | 0.07 | 0.00 |
| Sc | <1 | 18 | 1.00 | 0.00 | 1.00 | 1.00 | 0.00 |
| Se | <.5 | 0 | nd | nd | nd | nd | |
| Si | <40 | 18 | 3711.6 | 677.1 | 5236.0 | 2755.0 | 6.67 |
| Sm | <.02 | 4 | 0.02 | 0.00 | 0.03 | 0.02 | |
| Sn | <.05 | 0 | nd | nd | nd | nd | |
| Sr | <0.01 | 18 | 12.13 | 4.12 | 20.71 | 7.28 | 5.22 |
| Ta | <.02 | 0 | nd | nd | nd | nd | |
| Tb | <.01 | 0 | nd | nd | nd | nd | |
| Te | <.05 | 0 | nd | nd | nd | nd | |
| Th | <.05 | 0 | nd | nd | nd | nd | |
| Ti | <10 | 0 | nd | nd | nd | nd | |
| Tl | <.01 | 8 | 0.01 | 0.00 | 0.01 | 0.01 | 0.00 |
| Tm | <.01 | 0 | nd | nd | nd | nd | |
| U | <.02 | 0 | nd | nd | nd | nd | |
| V | <.2 | 3 | 0.20 | 0.00 | 0.20 | 0.20 | 0.00 |
| W | <.02 | 0 | nd | nd | nd | nd | |
| Y | <0.01 | 18 | 0.06 | 0.02 | 0.11 | 0.02 | 0.00 |
| Yb | <.01 | 12 | 0.01 | 0.00 | 0.01 | 0.01 | |
| Zn | <.5 | 17 | 4.15 | 2.56 | 9.30 | 0.70 | 9.03 |
| Zr | <.02 | 13 | 0.02 | 0.01 | 0.04 | 0.02 | 0.00 |
| TDS | | 18 | 8734.1 | 2645.8 | 16061.4 | 6217.2 | |
| ANC | | 17 | 41.82 | 25.46 | 95.00 | 9.00 | |
| pH | | 17 | 5.74 | 0.49 | 6.42 | 4.90 | |

**Table 3.** *Correlation coefficient matrix comparing major components of stream water in the Adirondack High Peaks region. Mono- and divalent cation concentrations are generally highly correlated but show strong negative correlations with trivalent cation concentrations.*

| r2 | Al | Ca | Fe | K | Mg | Mn | Na | Rb | Si | Sr | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Al | | –0.82 | 0.80 | –0.51 | –0.76 | 0.39 | –0.50 | –0.41 | –0.86 | –0.90 | 0.95 |
| Ca | | | –0.66 | 0.67 | 0.91 | –0.59 | 0.74 | 0.60 | 0.84 | 0.88 | –0.70 |
| Fe | | | | 0.05 | –0.59 | 0.89 | –0.27 | –0.51 | –0.8 | –0.60 | 0.79 |
| K | | | | | 0.77 | 0.37 | 0.45 | 0.88 | 0.60 | 0.50 | –0.36 |
| Mg | | | | | | –0.60 | 0.75 | 0.56 | 0.78 | 0.69 | –0.75 |
| Mn | | | | | | | –0.48 | 0.11 | –0.67 | –0.23 | 0.43 |
| Na | | | | | | | | 0.35 | 0.36 | 0.62 | 0.42 |
| Rb | | | | | | | | | 0.53 | 0.45 | –0.26 |
| Si | | | | | | | | | | 0.78 | –0.85 |
| Sr | | | | | | | | | | | –0.80 |
| Zn | | | | | | | | | | | |

## Results

Sample numbers JT-1 through JT-6 were not utilized; sampling numbering system begins at JT-7. Seventeen stream samples and one duplicate sample were analyzed.

*Elemental Analysis*

Stream samples from the High Peaks region (Table 1) were analyzed by ICP-MS for 72 elements (Table 2). Sixteen elements were detected above detection limits in all the stream samples analyzed (Table 2). Among those elements detected in all stream samples (Si), calcium (Ca), sodium (Na), magnesium (Mg), and aluminum (Al) had the highest concentrations in descending order. Quality control samples indicate that the data is accurate (comparison with actual standard values) and precise (comparison of replicate analyses). The relative percent difference (RPD) of standard values and replicate measurements varied systematically with concentration but was less than 10%, indicating that the data was of excellent quality. Iron was an exception with an RPD of 31.0% and was detected in only 7 of 17 samples.

The detection limit (DL) for each analyte, number of stream samples in which each element was found above detection limits (Count), the mean (Mean), standard deviation (SD), the range (High and Low), and the relative percentage difference (RPD) between certified and measured values of analytes in a wastewater standard are given (Table 2). For example, calcium was found above the detection limit (50 ppb) in all eighteen samples and had a mean concentration and standard deviation of 2076 ± 923 parts per billion (ppb). The range of measured values measured varied from 1061 to 4098 ppb. A RPD value of 9.09% was calculated for the difference between reported and measured values of the standard.

*pH and TDS*

The pH of the sampled stream water varied from 4.90 to 6.42 with a mean value of 5.74 ± 0.50. Much of the chemical variation appeared to be a function of pH. For example, Al concentrations in stream waters displayed an inverse relationship with pH, while Ca had a positive correlation (Table 3). TDS varied between 6.22 and 16.1 ppm with a mean of 8.9 ppm. However, since anions were not measured, actual TDS values are likely significantly larger. Total dissolved solids were also highly correlated ($r^2 = 0.78$) to pH (Table 3).

Acid neutralizing capacity measures the resistance of natural waters to acidification with a strong acid (Jenkins et al. 2007). The ANC values measured by Gran titration ranged between 25 and 95 μeq/L with a mean value of 41.8 μeq/L and also varied systematically with pH ($r^2 = 0.84$) and TDS ($r^2 = 0.88$). A mean value of 41.8 μeq/L indicates potential susceptibility to sporadic acidification because of minimal amounts of strong bases in the water, primarily Ca and Mg. Acidification events are primarily caused by the rapid release of acid species either during runoff from precipitation and/or during snowmelt.

*Meteorological Conditions*

While the precise meteorological and hydrological conditions at each sample location cannot be determined because of the lack of gauging stations in remote areas, estimates of the general conditions prior to and during the sampling events were available from nearby monitoring stations noted above. During the period one week prior to sampling the mean daily temperature ranged from 16.7 to 5.6°C. Three days prior to the sampling event 1.42 cm of rain was recorded at the Saranac Lake airport. This was followed by 0.38 and 0.20 cm on successive days. The hydrograph for the USGS gauging station at Ausable Forks shows a rise in discharge above long-term mean values, presumably related to rainfall over the High Peaks region with peaks in discharge just prior to sampling (Fig. 3). Discharge was approximately 33% greater than long-term averages for the sampling dates, indicative of enhanced runoff related to precipitation.

## Discussion

*Source of Dissolved Solids in High Peaks Streams*

Using the weight ratios of common cations and anions, Gibbs (1970) found that the composition of natural waters worldwide were dominated by three factors including precipitation, rock weathering, and vaporation/crystallization (Fig. 4). When TDS for High Peaks streams are plotted versus the weight ratio of Na/(Ca + Na) they fall (Fig. 4) outside of the region which encompasses

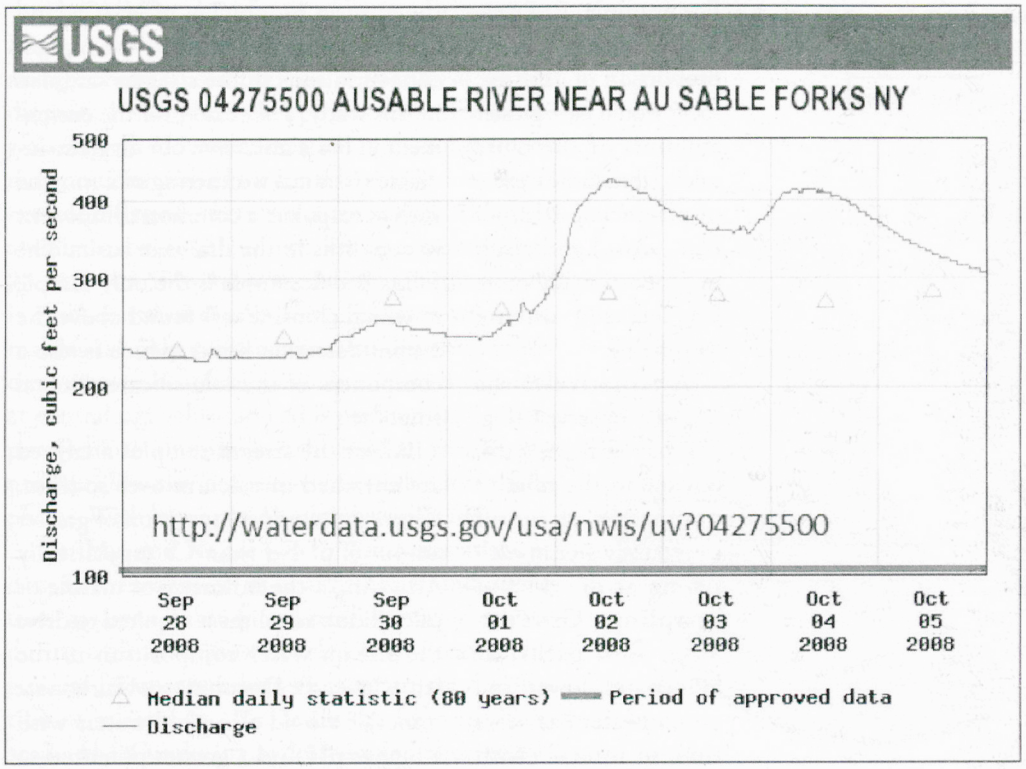


**Figure 3.** *Hydrograph showing the discharge recorded at the Ausable Forks USGS gauging station (#04275500) on the Ausable River for the period September 28 to October 5, 2008. Data from the website: http://waterdata.usgs.gov/usa/nwis/uv?04275500.*

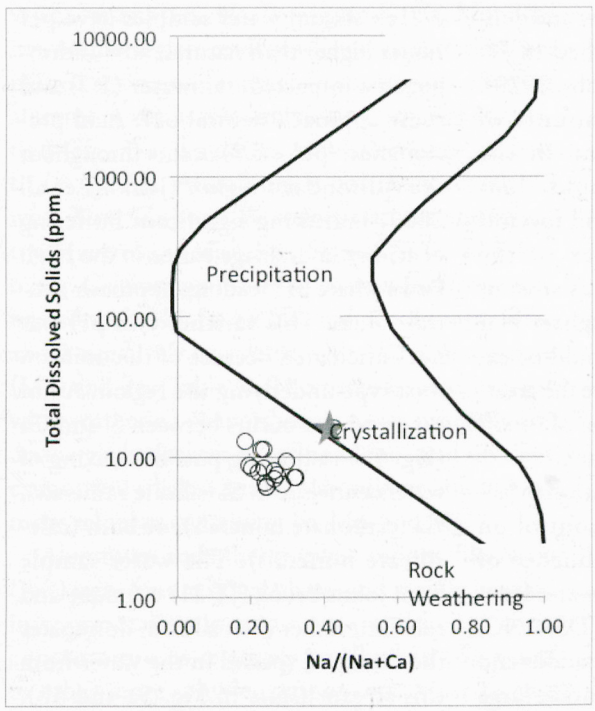


**Figure 4.** *Diagram which plots the total dissolved solids (TDS) versus the ratio of Na/(Na + Ca) for High Peaks streams sampled during this study (after Gibbs, 1970). The black line outlines the field of natural waters noted by Gibbs. The star indicates the sample from Johns Brook.*

the bulk of natural waters determined by Gibbs (1970). Even if the TDS values, which average 8.9 ppm, are doubled or tripled to account for anionic contributions they fall below of the range of most natural waters. Moreover, with one exception, they fall within the region noted by Eilers et al. (1992) for dilute lake waters in areas dominated by crystalline bedrock (e.g., Sierra Nevada, Maine, Minnesota, Norway).

High Peaks stream samples do not match other streams or rivers examined by Gibbs (1970) dominated by rock weathering or precipitation. High Peaks streams have lower TDS values than waters considered dominated by rock weathering and have lower Na/(Ca + Na) weight ratios than waters dominated by precipitation (Fig. 4). High Peaks stream samples form a tight cluster with the exception of sample JT-20 from Johns Brook. This sample has the highest TDS values and Ca, Mg, and Na concentrations measured and it plots substantially to the right of the main cluster of data (star, Fig. 4). It is inferred that the Johns Brook drainage basin contains a higher proportion of geologic materials with soluble components containing Ca, Mg, and Na.

The stream samples are relatively enriched in Ca compared to Na (Fig. 4); however, Na is more prevalent in precipitation. This enrichment in Ca observed in the High Peaks stream water samples is a clear indicator of the influence of rock weathering in dilute waters. TDS concentrations however, fall below those generally associated with rivers dominated by rock weathering and fall within and slightly above the upper range of those reported for precipitation (Eby, 2004; Gibbs, 1970). In contrast to most other regional studies, this study was carried out in drainage basins which are underlain by a single lithology (coarse crystalline massif anorthosite) devoid of minerals that readily dissolve (Eby, 2004). Despite sampling the streams in the headwater reaches of their respective drainage basins their chemistry suggests a strong influence from the underlying bedrock.

Cation data were used to construct a Piper plot (Piper, 1953), which uses a triangular diagram with the normalized concentrations of Ca, Mg, and Na. On the Ca-Mg-Na plot the High Peaks stream samples form a relatively tight, but linear cluster (Fig. 5a) with

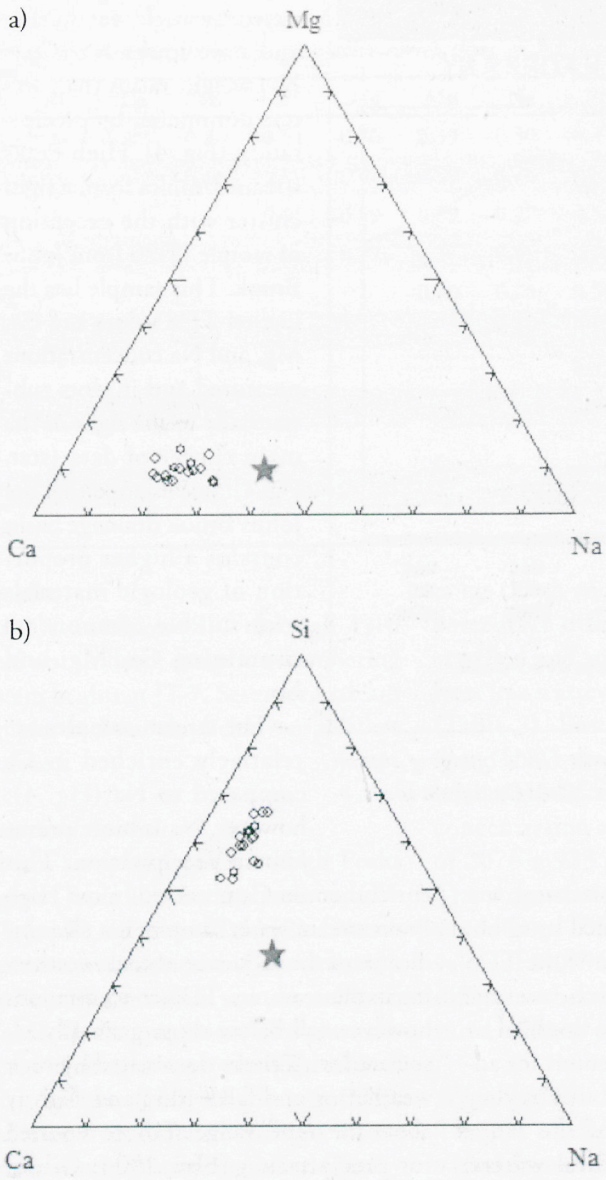


**Figure 5.** *Ternary diagrams (after Piper, 1953) plotting the normalized concentrations for High Peak streams: a) Ca, Mg, and Na b) Ca, Si, and Na. Stars indicate the sample from Johns Brook.*

consistent proportions of Mg. If this linear trend is a mixing line it connects sources with various proportions of Ca to Na but with similar amounts of Mg. Variability in Ca and Na is well documented among plagioclase feldspars in the High Peaks region (Fig. 1 of Casey et al. 1991) and the linear trend between Ca and Na could conceivably be a function of variable feldspar composition within various drainage basins. For example, drainage basins with a greater proportion of gabbroic rocks would have greater amounts of the more calcic labradorite variety of plagioclase feldspar ($An_{50}$–$An_{70}$) and result in proportionally more Ca released during weathering.

Alternatively, the linearity observed (Fig. 5a) may indicate a difference in the relative proportion of runoff to groundwater in each stream at the time of sampling. Groundwater flow paths are longer and slower, and groundwater has more time to interact with rock and therefore is more reflective of rock chemistry. Precipitation, which results in overland flow and runoff, is enriched in Na over Ca (Gibbs, 1970). Greater amounts of precipitation in the streams would elongate the trend towards the Na apex of the diagram, thus streams with the highest Na/Ca ratios would be expected to have the greatest proportion of runoff to groundwater.

One additional factor that may exert strong control on stream chemistry is the influence of soluble mineral phases. The water from Johns Brook has the highest TDS, ANC, and Ca, Mg, and Na concentrations and drains an area known to contain large marble and calc-silicate xenoliths (Isachsen & Fisher, 1970). The influence of highly soluble calcite would result in elongation of the cluster towards Ca; however, the Johns Brook sample has the greatest proportion of Na/Ca, and both elements are found at the highest concentrations in the streams sampled in this study. The reason for the enrichment in Na is unknown but may also indicate chemical weathering of a mineral such as scapolite, a common component in xenoliths in the drainage basin. The Johns Brook sample is the only sample in which chlorine was found above the 1 ppm detection limits, which is also a component of the calc-silicate mineral scapolite.

All of the stream samples analyzed are enriched in calcium over sodium. Given andesine's composition of greater amounts of Na than Ca (specifically $An_{30}$–$An_{50}$), the influence of marble or calc-silicate xenoliths is required to drive the stream water composition to the left (Ca–end). Dissolution of carbonate minerals would also yield waters with a higher pH and a greater potential to buffer acidity. Dissolution of calcite explains other water chemistry parameters observed including as high TDS, ANC, and Strontium (Sr) concentrations.

Ten stream water samples have pH values higher than natural, non-anthropogenic impacted, rainwater (5.7) and some approach neutral pH. Acid precipitation (pH < 5.7) occurs throughout the Adirondack region (Jenkins et al. 2007) indicating significant buffering of acidity in drainage basins in the High Peaks where pH readings approach neutral values. This variability in pH was not anticipated because of the uniform rock type underlying the region. A linear trend also occurs between Si and Ca (Fig. 5b) indicating possible mixing of waters enriched in Si (silicate minerals), Ca (carbonate minerals), or both (calc-silicate minerals). The water sample from Johns Brook (JT-21) is unique and calcium, rather than silicon, dominates the dissolved species in the water from this stream (stars in Fig. 5a and 5b). Knowledge of the detailed geology of individual drainage basins is needed to understand the geochemical variability observed, even within an area of relatively simple geology.

The relative abundance of major elements in High Peaks streams has many similarities to the average chemical composition of anorthosite (Buddington, 1939), the rock type that underlies the region (Fig. 6). However, variation in the solubility of major cations with pH is considerable and results in notable differences between them as well. Although aluminum oxide (Al2O3) makes up approximately 25.61% (13.55% Al) of the Marcy anorthosite; Al is much less abundant in High Peaks stream water, making up only 4.3% of the total dissolved solids on average. The solubility of aluminum is very low at neutral pH values and Al is preferentially incorporated into aluminum-rich, residual weathering products like clay or relatively insoluble hydroxide phases. With lower pH Al solubility increases.

Ca, Mg, and Na are two to four times as abundant in stream waters as in anorthosite, indicating their greater solubility and relatively rapid release during hydrolysis (Casey et al. 1991). Because plagioclase feldspar weathers by incongruent dissolution, it releases Ca, Na, Si (in the form of silicic acid—$H_4SiO_4$) during hydrolysis, and alters to hydrous, aluminous phyllosilicate mineral phases such as kaolinite or gibbsite.

The difference in the behavior of trivalent, insoluble cations (i.e. Al, Fe) and soluble mono- and divalent cations (i.e., Na, Potassium-K, Ca, Mg) during weathering are evident when concentrations are plotted against one another on scatterplots. Plotting aluminum versus calcium yields a negative correlation (Fig. 7) and a power correlation gives the best fit ($r^2$ = 0.82). Aluminum is positively correlated with Zinc (Zn) and Fe concentrations and negatively correlated with Mg, Si, and Sr, in addition to Ca. Calcium on the other hand is positively correlated with Mg, Sr, Si, Na, and K concentrations, and is negatively correlated with Al, Fe, manganese (Mn) and Zn (Table 3). These trends are consistent with weathering of anorthositic rocks, primarily andesine via hydrolysis releasing mono- and divalent cations and silicic acid and subordinate amounts of mafic minerals containing Fe, Mn, and Mg.

Aluminum and other trivalent cations, like ferric ($Fe^{3+}$) iron, form residual phases and rapidly increase in concentration in acidic waters, although their concentration is relatively small when compared to other more soluble components. Most Fe and Mn is likely derived from the weathering of ferrous ($Fe^{2+}$) silicate minerals like biotite, pyroxene, and hornblende, Al and Si are key components of feldspar. K was found above the detection limit of 50 ppb in only 11 of 17 samples and its relatively low

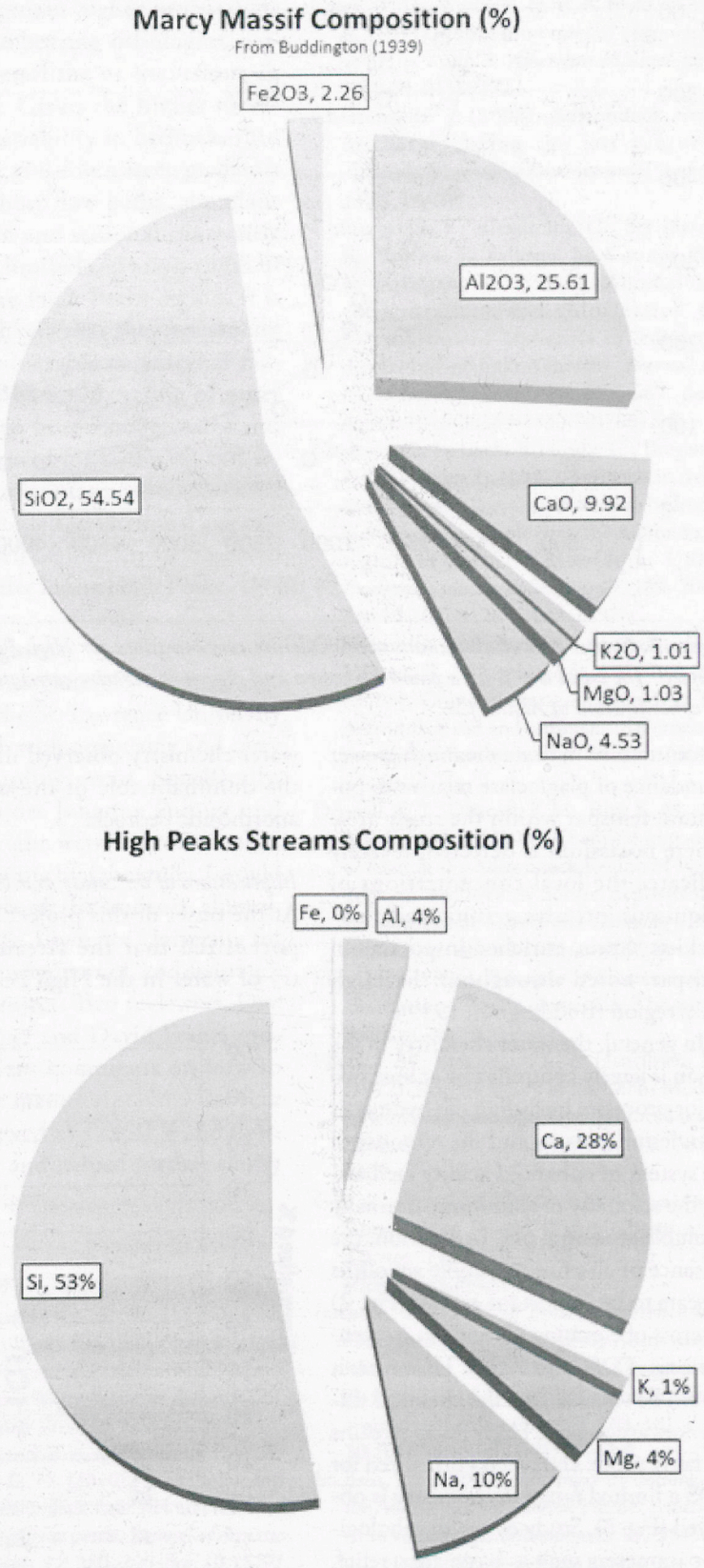


**Figure 6.** *Pie chart showing the normalized abundance of the major cationic components of anorthosite (Buddington, 1939) and High Peaks Stream water composition. Rock chemistry is given in oxide percentages and water chemistry in normalized elemental concentrations.*

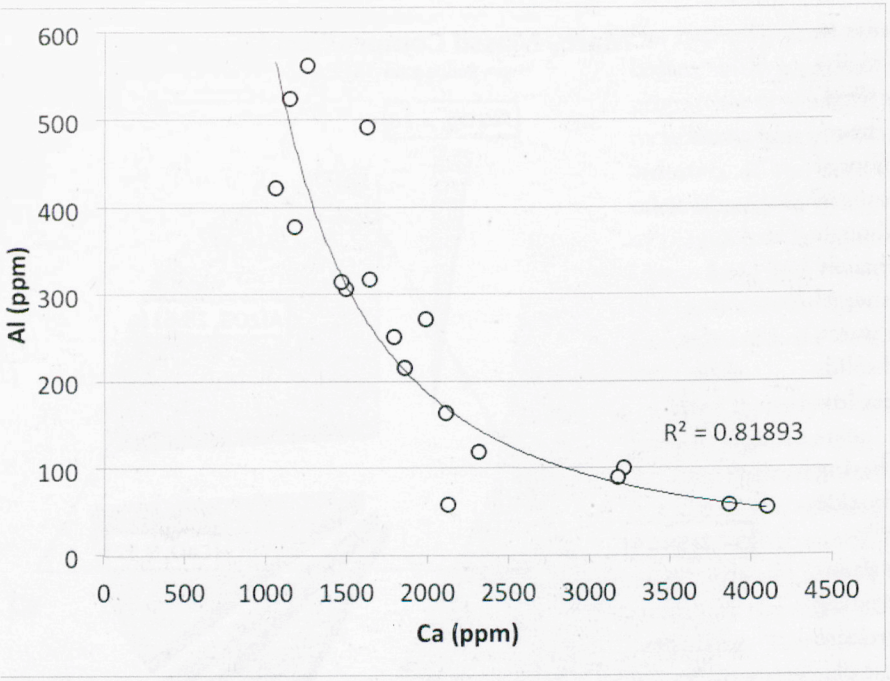


**Figure 7.** *Scatter plot of aluminum versus calcium concentrations for High Peaks streams sampled. The trend line is for a power regression and suggests a negative correlation between the concentration of Al and Ca.*

concentrations indicate the much greater abundance of plagioclase relative to potassium feldspar within the study area. Where potassium is detected, it likely indicates the local concentrations of ubiquitous intrusive granitic and charnockitic sheets, enriched in potassium feldspar, noted throughout the High Peaks region (Buddington, 1939).

In general, the water chemistry in the region is largely controlled by at least two major processes including the hydrolysis of andesine feldspar and the response of the system to enhanced acidity facilitating the solubility of aluminum, normally insoluble at neutral pH. In addition, the presence or absence of soluble xenoliths appears to be important as well (Fig. 2) in terms of elevating Ca and Na concentrations, TDS, and ANC. However, it should be stressed that the chemical differences among the High Peaks streams are fairly subtle and when normalized for TDS a limited range in chemistry is observed (Fig. 8). Study of geomorphological parameters such as basin area, relief, slope, and stream order, among others may help further refine the preliminary interpretations presented here; however, the relatively limited variation in stream water chemistry observed underscores the dominant role of the underlying anorthositic bedrock.

*Implications of the Study and Future Work*

At the onset of this project it was hypothesized that the stream chemistry of water in the High Peaks region would be most strongly influenced by precipitation. The reasons for this hypothesis are numerous and include the lack of local anthropogenic activity, limited soil development, minor amounts of unconsolidated sediment blanketing bedrock, short and fast overland flow paths down steep terrain, minimized weathering due to harsh climatic conditions and limited forest development, the resistance of coarse-grained, nearly monomineralic, metaigneous rock to weathering (limited porosity and permeability), and relatively high amounts of precipitation. Precipitation may well strongly control some of the anionic species not measured in this study including $SO_2$ and $NO_x$ or mercury and other contaminants with limited sources within the Adirondack region. It is clear, however, that the bedrock in the Adirondack High Peak region has a strong influence on the multi-element chemistry, pH, and ANC of streams in the study area.

Relatively little detailed study has occurred on the acidification of streams in the Adirondack region with the exception of the western Adirondacks (Lawrence, 2002, Lawrence et al. 2004; 2008). In the western Adirondacks both

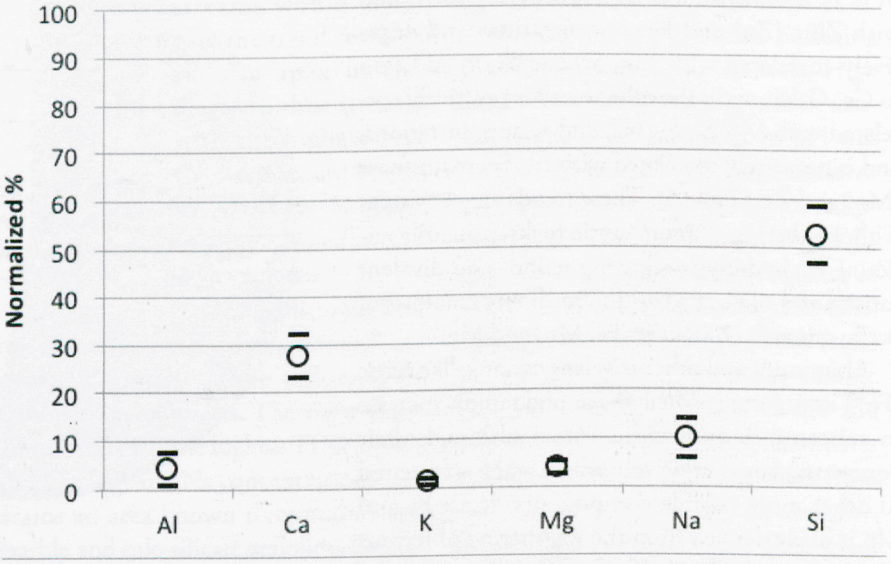


**Figure 8.** *Plot of normalized major element concentrations or each of the High Peaks streams sampled. A filled circle indicates mean percentage of total for each element and upper and lower bars indicate standard deviation of entire dataset. This diagram shows the limited range in stream composition when differences in TDS are normalized.*

chronic and episodic acidification has been recognized as problematic. Little or no work has occurred in the High Peaks region but the limited number of geological variables makes it an ideal area to study subtle differences in headwater drainage basins and their response to acidification. In addition, because of the limited potential for storage of acidic species in shallow soils and the rapid flow-through of water, these drainage basins should respond quickly to any changes in wet or dry deposition of contaminants and thus represent a potential opportunity to observe and monitor changes in water chemistry that will eventually affect the entire region.

While this study underscores the need for detailed understanding of the bedrock geology and its influence on stream water chemistry, additional monitoring of stream chemistry in the High Peaks region is needed. Key anions and mercury should be added to the analyte list for a more complete picture of the deposition of far-traveled atmospheric contaminants. Studies involving seasonal or event sampling are of high importance, as well buffered streams can become periodically acidic and impact biota (Lawrence, 2002). And finally, evaluation of geomorphological parameters such as slope, relief, drainage basin size, etc., that control the interaction of water with geologic materials within a drainage basin, will allow a more detailed understanding of the factors controlling stream water chemistry.

## Conclusion

A preliminary study of baseline stream water chemistry in the High Peaks region indicates that the water is slightly acidic, dilute, and dominated by silicon and calcium. Other important constituents include sodium, magnesium and aluminum, indicating the primary control on stream water chemistry is the chemical weathering of anorthosite bedrock by hydrolysis. Samples with the highest total dissolved solids, pH, acid neutralizing capacity, calcium, and strontium occur in drainage basins known to contain higher proportions of carbonate-bearing lithologies, primarily as xenoliths or inclusions in anorthosite. Given the higher elevations, low variability in bedrock, thin and sporadic soil cover, steep gradients and relief, short flow paths, abundant precipitation and seasonal snow melt inputs, and limited retention times of steams in the High Peaks region, it is considered likely that they are among the most vulnerable to external factors. Given the rapid cycling of water through these headwater streams and limited potential for buffering and sequestration of contaminants, potential changes in baseline chemical parameters may well be initially be observed in stream water in the High Peaks.

## Acknowledgments

I would like to gratefully acknowledge the help of the St. Lawrence University Outing Club with organizing and carry out the sampling event. Specifically, geology majors Johanna Palmer and Thomas Wright were instrumental in coordinating much of the study. I would also like to thank the students, alumni, and staff of St. Lawrence University for their generous support of, and assistance with, this project. Two reviewers, Drs. Robert Badger and David Franzi provided excellent comments on how to improve the manuscript. Ms. Rebecca Steinberg served as a capable and thorough editor and helped further clarify the manuscript.

## References

Baker, J. P., Warren-Hicks, W. J., Gallagher, J., & Christensen, S. W. (1993). Fish population losses from Adirondack lakes: The role of surface water acidity and acidification. *Water Resources Research, 29,* 861–874. doi: 10.1029/92WR02329

Brown, D., Goncharov, A., Simonin, P. E., & Carpenter, D. O. (2010). The relationship between Adirondack Lake pH and levels of mercury in yellow perch. *Journal of Aquatic Animal Health, 22,* 280–290. doi: 10.1577/H10-005.1

Buddington, A.F., (1939). Adirondack igneous rocks and their metamorphism: *Geological Society of America Memoir 7,* 1–354.

Casey, W. H., Westrich, H. R. & Holdren, G. R. (1991). Dissolution rates of plagioclase at pH = 2 and 3. *American Mineralogist, 76*(1–2), 211–217.

Chiarenzelli, J. (2008). Adirondack river discharge during the last century. *Adirondack Journal of Environmental Studies, 14*(2), 14–21.

Chiarenzelli, J., Alexander, C., Scrudato, R., Pagano, J., Falanga, L., Connor, B., & Milligan, M. (2002). Anomalous concentrations and chlorination of polychlorinated biphenyls in sediment downwind of Lake Ontario. *Journal of Great Lakes Research, 28,* 674–687. doi. org/10.1016/S0380-1330(02)70613-8

Chiarenzelli, J., Lock, R., Cady, C., Bregani, A. & Whitney, B. (2012). Variation in river multi-element chemistry related to bedrock buffering: an example from the Adirondack region of northern New York, USA. *Environmental Earth Sciences 67,* 189–204. doi: 10.1007/s12665-011-1492-z.

Chiarenzelli, J., Pagano, J., Milligan, M., Holsen, T., Glovak, J. & Althouse, K. (2006). Contaminant concentrations in Adirondack soil and sediment. *Adirondack Journal of Environmental Studies, 13*(2), 34–40.

Driscoll, C.T., Driscoll, K.M., Roy, K. M., & Mitchell, M. J. (2003). Chemical response of lakes in the Adirondack Region of New York to declines in acidic deposition. Environmental. *Science and Technology, 37,* 2036–2042. doi: 10.1021/es020924h

Eby, G. N. (2004). *Principles of Environmental Geochemistry.* Pacific Grove, CA: Thomson Brooks/Cole.

Eilers, J. M., Brakke, D. T., & Henriksen, A. (1992). Inapplicability of the Gibbs Model of world water chemistry to dilute lakes: *Limnology and Oceanography, 37*(6), 1335–1337.

Gibbs, R. J. (1970). Mechanisms Controlling World Water Chemistry: *Science, 17,* 1088–1090. doi: 10.1126/science.170.3962.1088

Isachsen, Y.W. (1975). Possible evidence for contemporary doming of the Adirondack Mountains, New York, and suggested implications for regional tectonics and seismicity: *Tectonophysics, 29,* 169–181, doi: 10.1016/0040-1951(75)90142-0.

Isachsen, Y.W. (1981). Contemporary doming of the Adirondack Mountains: Further evidence from releveling: *Tectonophysics, 71,* 95–96. doi: 10.1016/0040-1951(81)90051-2.

Isachsen, Y. W. & Fisher, D. W. (1970). *Geologic map of New York State, Adirondack Sheet* (1:250,000 scale), New York State Science Service Map and Chart Series 16.

Jenkins, J., Driscoll, C., Roy, K., & Buerkett, C. (2007). *Acid rain in the Adirondacks: an environmental history* (1st ed.). Ithaca, NY: Cornell University Press.

Jenkins, J. & Keal, A. (2004). *An Adirondack Atlas: A Geographic Portrait of the Adirondack Park.* Syracuse, NY: Adirondack Museum/ Syracuse University Press.

Kretser, W. A., Gallagher, J., & Nicolette, J. (1989). *Adirondack lakes Study 1984–1987: An evaluation of fish communities and water chemistry.* Raybrook, NY: Adirondack Lakes Survey Corporation.

Lawrence, G. B. (2002). Persistent episodic acidification of streams linked to acid rain effects on soil. *Atmospheric Environment, 36,* 1589–1598. doi:10.1016/S1352-2310(02)00081-X

Lawrence, G. B., Baldigo, B. P., Roy, K. M., Simonin, H.A. & Bode, R. W. (2008). *Results from the 2003–2005 Western Adirondack Stream Survey.* Albany, NY: New York State Energy Research and Development Authority.

Lawrence, G. B., Momen, B. & Roy, K. M. (2004). Use of stream chemistry for monitoring acidic deposition effects in the Adirondack Region of New York. *Journal of Environmental Quality, 33*(3), 1002–1009.

McKibben, B. (2002). Future shock: the coming Adirondack climate. *Adirondack Life,* March/April 2002, 51–57.

McLelland, J., Chiarenzelli, J., Whitney, P. & Isachsen, Y. (1988). U-Pb zircon geochronology of the Adirondack Mountains and implications for their geologic evolution. *Geology, 16,* 920–924. doi 10.1130/0091-7613(1988) 016<0920:UPZGOT> 2.3.CO;2

McLelland, J., Daly, S. & McLelland, J.M. (1996). The Grenville Orogenic Cycle (ca. 1350–1000 Ma): An Adirondack perspective. *Tectonophysics, 265,* 1–28. doi. org/10.1016/S0040-1951(96)00144-8

McLelland, J.M., Selleck, B.W. Hamilton, M. & Bickford, M.E. (2010). Late- to post-tectonic setting of some major Proterozoic Anorthosite-Charnockite-Mangerite-Granite (AMCG) Suites. *Canadian Mineralogist, 48,* 1025–1046. doi 10.3749/canmin.48.4.000

Piper, A.M. (1953). A Graphic Procedure in the Geochemical Interpretation of Water Analysis. *Transactions, American Geophysical Union, 25,* 914–928. doi: 10.1029/ TR025i006p00914

Regan, S. P., Chiarenzelli, J. R., McLelland, J. M. & Cousens, B. L. (2011). Evidence for an enriched asthenospheric source for coronitic metagabbros in the Adirondack Highlands. *Geosphere, 7,* 694–709. doi: 10.1130/GES00629.1

Roden-Tice, M. K.& Tice, S. J. (2005). Regional Scale Mid-Jurassic to Late Cretaceous Unroofing from the Adirondack Mountains through Central New England based on Apatite Fission-Track and (U-Th)/ He Thermochronology. *Journal of Geology, 113,* 535–552.

Schneider, Paul (1997). *The Adirondacks, a History of America's First Wilderness.* New York, NY: Henry Holt and Company.

Stager, J.C. & Martin, M. R. (2002). Global climate change and the Adirondacks. *Adirondack Journal of Environmental Studies, 9,* 1–10.

Taylor, J. P. & Fitzgerald, P. G. (2011). Low-temperature thermal history and landscape development of the eastern Adirondack Mountains, New York: Constraints from apatite fission-track thermochronology and apatite (U-Th)/He dating: *Geological Society of America Bulletin, 123,* 412–426. doi: 10.1130/B30138.1

Terrie, Phillip G. (1997). *Contested Terrain: A New History of Nature and People in the Adirondacks,* Syracuse, NY: Adirondack Museum/Syracuse University Press.

KEN RIMANY

*Storm front approaching at twilight*